



# An assessment of procedures to remove exogenous Sr before $^{87}\text{Sr}/^{86}\text{Sr}$ analysis of wet archaeological wool textiles



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## ABSTRACT

Strontium isotope analysis ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) has been employed as a provenancing tool for archaeological wool textiles. To date, the effect of post-depositional (soil burial environment) contamination on keratin samples, which contain ~ppm concentrations of Sr, has not been rigorously investigated. We compared published methods for removing exogenous Sr from keratinous textiles, using either: (1) compressed  $\text{N}_2$  gas, (2)  $\text{HF}(\text{aq})$  solution (with and without a strong oxidising agent to remove dyestuff) or (3) organic solvents.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr contents were determined in undyed and madder-dyed/alum-mordanted moieties of the same wool textile, buried for up to three years in contrasting environments (marine sediment/fenland bog), and two archaeological textiles recovered in Iceland (one typical and one atypical of local manufacture). Undyed experimental samples had low Sr contents (0.07–0.29 ppm) that were increased by both dyeing (0.14–8.92 ppm) and soil burial (0.11–15.01 ppm). The efficacy of Sr removal was:  $\text{HF}(\text{aq}) + \text{oxidising agent} > \text{organic solvents} > \text{HF}(\text{aq}) > \text{compressed } \text{N}_2$ . Unburied samples showed little variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio between cleaning methods (0.00006–0.00035); buried samples showed greater variation (0.00257–0.00713). Archaeological samples showed Sr contents greater than experimental soil burials (1–118 ppm), and  $^{87}\text{Sr}/^{86}\text{Sr}$  values consistent with Icelandic groundwater (0.70357–0.70540). No cleaning methods retrieved original (unburied and undyed)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios except treatment with compressed  $\text{N}_2$  in undyed samples. Exogenous Sr from the short term soil burial environment is probably mostly present as particulates. We conclude that  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of archaeological wool textiles recovered from wet burial environments do not accurately reflect wool provenance even after cleaning with the methods investigated.

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## 1. Introduction

Wool textiles are a class of cultural material widespread in the historic and prehistoric past (e.g. Bender Jørgensen, 1992; Munro, 2003; Walton Rogers, 2007). A method to establish the provenance of archaeological textiles recovered from wet archaeological deposits would expand our knowledge of the movement of their raw materials, as well as that of these objects of considerable economic, artistic, technological and social importance (Schneider, 1987). Sr isotope provenancing has proved exceptionally useful to discriminate local from non-local in human and animal

archaeological remains (Bentley, 2006; Chenery et al., 2010; Viner et al., 2010), in modern human forensic studies (Aggarwal et al., 2008; Font et al., 2012) and in ecological studies (Ben-David and Flaherty, 2012; Hobson, 1999) including in modern bird feather keratins (Evans and Bullman, 2009; Font et al., 2007; Sellick et al., 2009). The technique has been extended to finds of archaeological wool textiles (Frei et al., 2009a, Frei, et al., 2009b, Frei, et al., 2010, von Carnap-Bornheim et al., 2007). These studies did not, however, directly test the effect of diagenesis under soil burial conditions, a process which is known to overprint the Sr isotope signature in bone on archaeological timescales (e.g. Trickett et al., 2003).

Mammalian hairs are structurally, thermodynamically, mechanically and biochemically very similar to each other (Popescu and Höcker, 2009; Wortmann, 2009). They are composite but strongly proteinaceous tissues (90–97% dry mass), which also contain 2–8% melanins, and 2% lipids. The protein fraction consists

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of a mixture of over a hundred proteins, mostly keratins (e.g. Clerens et al., 2010; Lee et al., 2006). The distribution of these proteins, and their crosslinking, varies between the different structures of the fibre (filament, matrix, medulla, cuticle: Koehn et al., 2010; Plowman et al., 2007). Wool is typically finer than human hair, with a much thinner cuticle (Wolfram and Lindemann, 1971), and contains slightly less integral lipid per unit mass (Wert and Downing, 1989). In contrast to human hair, fibres in wool textile are likely to have been extensively processed, both mechanically (e.g. combing, spinning, weaving, felting) and chemically (e.g. scouring to remove lipids, bleaching, dyeing/mordanting, fulling), and may have been in use (and hence exposed to chemical or UV alteration: e.g. Dyer et al., 2010) for a significant number of years before burial.

Wool has a known affinity for heavy metal cations (Popescu and Wortmann, 2010) for which it is used industrially as a sequestering agent (e.g. Homonoff et al., 2001). Archaeological and experimentally degraded human hair and sheep wool have been shown to absorb metal ions from the environment (Kempson et al., 2003; Kempson et al., 2010; Peacock, 1996), including bivalent  $\text{Ca}^{2+}$  that is a proxy for  $\text{Sr}^{2+}$ , having similar mass and size and the same valence state. The same is likely to occur in traditional methods of dyeing wool fibres, which involve heating wool in the presence of both a dyestuff and a mineral complexing agent (mordant) to bind the dye molecule to the fibre (Ferreira et al., 2004). Solvent cleaning methods to removal metal cations from keratinous material differ in efficiency for different elements (Borella et al., 1996; Chittleborough, 1980; Morton et al., 2002), with individual element behaviour at least partially dependant on pH (Hawkins and Ragnarsdóttir, 2009; Kar and Misra, 2004). Therefore the Sr content of archaeological wool textiles may reflect exogenous contributions to, or partial removal of endogenous Sr from the fibre, due to pre-burial processing, dyeing and mordanting, groundwater in the soil burial environment and post-excavation cleaning. These processes may obscure the original provenance signal of the fibre.

Solvent cleaning methods for Sr analysis in keratins will affect metal ions differently, depending on the nature of the binding of the metal ions to the fibre. This has been characterised in terms of interior/exterior binding for human hair (Tippie et al., 2013). Given the permeability of keratin fibres to water (Popescu and Höcker, 2007) and metal ions (see above), it is unlikely that this model adequately describes either the deposition of exogenous Sr into wool fibres from solution or the removal of endogenous or exogenous Sr from wool fibres by solvent cleaning methods. The most probable mechanism for long-term entrapment of metals in wool is reaction with the abundant cysteine residues in the keratin associated proteins (KAPs) to form stable metal mercaptides, and ultimately the precipitation of nano-crystalline metal sulphides (a Greco-Roman hair-dyeing method: Walter et al., 2006). Metals may also bind to exchangeable (pH reversible) sites, most likely free carboxyl groups of acidic amino acids in KAPs and intermediate filament proteins, and in melanins (Morton et al., 2002). The relative abundance of binding sites will change as the hundreds of different proteins present in wool fibres (Clerens et al., 2010) decay at different rates under burial conditions (Wilson et al., 2007). Sr is also present in the lipid (Attar et al., 1990) and melanin (Hawkins and Ragnarsdóttir, 2009) fractions of hair, which respond differently from proteins in soil burial conditions (Wilson et al., 2007). It is therefore likely that the Sr content of keratin fibres will be differently affected by cleaning methods which vary in pH, polarity and oxidising strength.

This study examines the effect of soil burial in wet environments on Sr isotopic composition and elemental abundance in dyed and undyed wool textile samples. It compares the effects of four methods employed for cleaning keratin fibres for Sr isotope

analysis: high pressure  $\text{N}_2$  (Font et al., 2007); 20% HF(aq) (Frei et al., 2009b), with and without the addition of ammonium persulfate, a strong oxidising agent (Frei et al., 2010); and a methanol/dichloromethane mixture and water (preparation procedure for light stable isotope analysis; adapted from Hedges et al., 2005). We hypothesised that if endogenous Sr in wool binds primarily to:

- pH-sensitive exchangeable sites on the protein or cysteine residues, HF(aq) cleaning should remove it but not treatment with compressed  $\text{N}_2$  or organic solvents;
- endogenous lipids, organic solvents should remove it, as should treatment with HF(aq), but not compressed  $\text{N}_2$ ;
- particulates, all cleaning procedures should remove it, but only  $\text{N}_2$  cleaning should remove only this contaminant.

## 2. Experimental approach

The overall experimental design is shown in Fig. 1.

### 2.1. Sample origin

One section of a highly fulled twill wool textile in non-pigmented fibre (Norwegian: *vadmel*; Røros Tweed A/S, Røros, Norway) was dyed by immersion in hot water containing commercially obtained dried madder root and alum powder (Nielsen, 1972, 106), in the Textile Workshop at “Land of Legends Lejre” (formerly Historical-Archaeological Research Centre Lejre, Denmark) with a resulting colour that was homogenous to the eye (photographs in Solazzo et al., 2013). Dyeing with madder root and a mineral mordant such as alum was a widespread wool colouring method in Europe from at least the Iron Age until the development of synthetic alizarin dyestuff in the 19th century (Chenciner, 2000; Vanden Berghie et al., 2009; Walton, 1991). Manufacturers' details for the materials and equipment used in the dyeing process were not available.

Samples of the dye/mordant treated material and samples of an undyed section of the same textile were buried in contrasting temperate soil environments by Elizabeth E. Peacock and colleagues (Bergstrand and Nyström Godfrey, 2007; Peacock, 2004; Turner-Walker and Peacock, 2008) and recovered after 1–8 years. Burial site characteristics are described in Table 1. The effect of degradation on wool fibres in these samples has been characterised

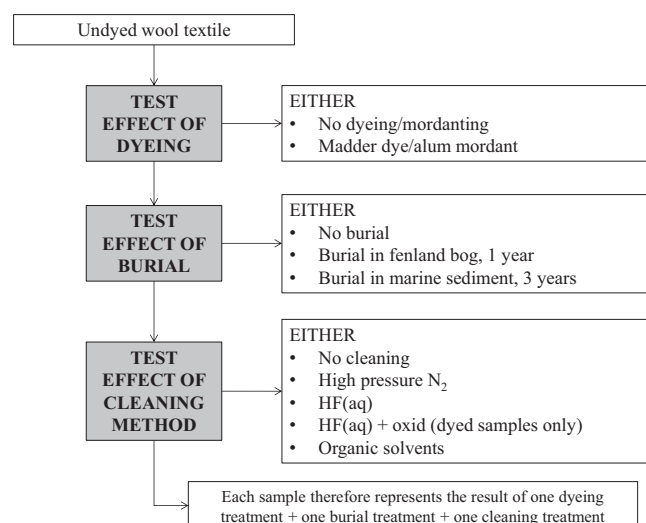


Fig. 1. Schematic of sample treatment.

**Table 1**

Environmental variables for experimental burial sites (Bergstrand and Nyström Godfrey, 2007; Solazzo et al., 2013; Turner-Walker and Peacock, 2008).

	Marine sediment	Raised bog
Location	Marstrand Harbour, Sweden	Rørmyra Nature Reserve, Bymarka, Sør-Trondelag County, Norway
Topography	Marine harbour (in use)	Raised bog, subarctic climate, below wooded upland
Geology	Marine sediment (some anthropogenic contribution)	Glacial till
Latitude	57.88678°	63.525°
Longitude	11.58732°	10.29722°
Elevation	0 m	175 m
Soil water pH	7.2–7.5	5.0
Soil water $E_h$	NA	+152 ms
Dissolved O <sub>2</sub>	<0.01 mg dm <sup>-3</sup>	1.6%
Average annual air temp.	7.4 °C	3.3 °C
Average annual temp at 1 m	NA	4.2 °C
Water content	33%	100%
Reducing potential	–160 to –250 mV (vs. standard hydrogen electrode).	–
Sediment nature	Fine sand, organic matter content <5%. Reducing environment below 50 cm and low water content. Organic matter content 5–7%.	“Almost pure sphagnum peat, with visibly well-preserved vegetable matter including small twigs and leaves” “Spectacular preserving qualities of sphagnum moss” due to sphagnum “Inhibits microbial action by deactivating proteolytic enzymes and binding free amino groups, thus denying micro-organisms access to nutrition”

proteomically (Solazzo et al., 2013) and via amino acid, elemental and light stable isotopic composition (von Holstein et al., 2014).

In addition to the soil-buried samples, archaeological wool textiles 2000-6-187(b) and 1989-33-380(f) were selected from the 13–14th and 15–16th century phases, respectively, of the assemblage at Reykholt, Borgarfjörður, Iceland (Walton Rogers, 2012). To stabilise them after excavation, these finds were rinsed in Icelandic tap water and allowed to air-dry at room temperature, before being packaged in inert materials (P. Walton Rogers, The Anglo-Saxon Laboratory, pers. comm.). No consolidants or other chemical treatments were applied. Textile 2000-6-187(b) was identified as of Icelandic origin, and 1989-33-380(f) as probably of mainland European manufacture, on art-historical/technical grounds. This identification was supported by light stable isotope analysis (von Holstein, 2012). The young basaltic volcanic rocks of Iceland yield some of the lowest groundwater <sup>87</sup>Sr/<sup>86</sup>Sr ratios in Europe (range 0.7035–0.7055: Voerkelius et al., 2010), though values from samples of animal and vegetable origin indicate a contribution from marine sources (range 0.7045–0.7080: Evans and Bullman, 2009; Price and Gestsdóttir, 2006; Voerkelius et al., 2010). It is nevertheless highly unlikely that the European import had such low <sup>87</sup>Sr/<sup>86</sup>Sr values.

## 2.2. Reagents

35% nitric acid (HNO<sub>3</sub>) and 20% hydrofluoric acid (HF(aq)) were purified by sub-boiling distillation in PTFE from initial *pro analysi* > 65% HNO<sub>3</sub> (Sigma–Aldrich, St Louis, MO, USA) and analysis grade 40% HF (Merck, Darmstadt, Germany). 22–26% hydrochloric

acid (HCl) was purified by sub-boiling distillation in quartz equipment from initial *pro analysi* > 37% HCl (Sigma–Aldrich, USA). 31% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) of ultra pure quality (Merck), and ammonium persulfate (*pro analysi*, Merck) were used for removal of organic material. Organic solvents dichloromethane (DCM) and methanol (MeOH), both HPLC grade (Fisher Scientific, Loughborough, UK), were used for sample cleaning. Ultra pure water (resistivity >18 MΩ) used throughout the chemistry procedure and for dilution of concentrated acids was obtained from a Milli-Q element system (Millipore, Billerica, MA, USA).

## 2.3. Sample cleaning

Five aliquots of up to 0.7 g of experimentally buried and archaeological wool were taken from each textile sample/find, and each was processed using one of the methods in Table 3. Due to small sample sizes remaining after burial, no experimental replicates were made. Larger sample sizes were available for the unburied controls; these were used whole (rather than as multiple replicates) in the expectation of very small Sr yields. Treatment with compressed N<sub>2</sub> and organic solvents was carried out at Bio-Arch, York, UK under standard laboratory conditions. Both HF cleaning methods and all dissolution and spiking procedures were carried out under clean lab conditions (Class 100) at the Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam (VUA), The Netherlands.

Samples cleaned with N<sub>2</sub> were secured in a small plastic container on PTFE mesh, and exposed to multiple 30-s blasts of high pressure N<sub>2</sub> gas (oxygen-free nitrogen, Linde Group, Munich, Germany). Samples cleaned with HF were placed in 7 mL Teflon screw-cap beakers (Savillex™, Minnetonka, USA) and exposed to 0.5–6 mL 20% HF(aq) for 60 min in the case of experimentally buried textiles, or 30 min in the case of archaeological textiles (following Frei et al., 2009b). In selected experiments, 3 mL 0.2 M ammonium persulfate solution was added at the same time as the HF. The supernatant solution was then removed by pipette and the sample rinsed 2–3 times with 1 mL Milli-Q water. The combined rinsing solution and supernatant was retained for analysis. Samples cleaned with organic solvents were sonicated with mixtures of DCM and MeOH, and with Milli-Q water (based on the protocol in Hedges et al., 2005), using a test sieve (Endecotts Ltd, London, UK; aperture 63 µm) to retain any sample fragments.

## 2.4. Sample dissolution

All samples were placed in 7 mL Teflon screw-cap beakers, and a highly enriched (>99.9%) <sup>84</sup>Sr spike (0.03–0.28 g, depending on sample mass) was added. To remove organic compounds, 1:1 v/v mixtures of 35% HNO<sub>3</sub> and 31% H<sub>2</sub>O<sub>2</sub> were added to each sample for closed-vessel digestion. Samples did not dissolve within 30 min as described previously (Frei et al., 2009b), even with heating on a hotplate at 90 °C. The samples were therefore subjected to successive 30 min ultrasonication and digestion on a hotplate at 110–140 °C with (1) 50% HNO<sub>3</sub>; (2) 4:1 v/v mixture of 50% HNO<sub>3</sub> and 31% H<sub>2</sub>O<sub>2</sub>; (3) 22–26% HCl; (4) 3:1 v/v mixture of 22–26% HCl and 50% HNO<sub>3</sub> (Font et al., 2007) until samples were completely dissolved (up to 6 days). The red colouration in all dyed samples had faded within 24 h, and most samples had been digested at this point. The solutions were dried and taken up with 0.5 mL 50% HNO<sub>3</sub> and loaded onto cleaned quartz columns containing preconditioned Sr-Spec™ resin (100–125 µm) suspended in Milli-Q water (Horwitz et al., 1992). After several washes with 20% HNO<sub>3</sub>, Sr was eluted in Milli-Q water and dried before final nitration in 88% HNO<sub>3</sub>.

**Table 2**

Sample descriptions: origin, burial site and pre-burial treatment.

Sample no	Sample type	Origin	Geology of origin	Site of burial	Geology of burial site	Approx. soil $^{87}\text{Sr}/^{86}\text{Sr}$	Burial period/y	Dye/mordant
1	Control	Rørøs, NO	Caledonian nappe complexes	N/A	N/A	Unknown	0	None
2	“	“	“	“	“	“	“	Madder/alum
3	Experimentally buried	Rørøs, NO	Caledonian nappe complexes	Lejre, DK	Quaternary drift	0.7076–0.7096* 0.7093–0.7105 <sup>§</sup>	1**	None
4	“	“	“	“	“	“	“	Madder/alum
5	“	“	“	Marstrand, SE	Marine sediment	0.7092 <sup>†</sup>	3	None
6	“	“	“	“	“	“	“	Madder/alum
7	Archaeological	Unknown (Icelandic)	Tertiary or Quaternary volcanic rock	Reykholt, Iceland	Tertiary volcanic rock >3.1 mya	0.7035–0.7055 <sup>‡</sup>	c. 500	Unknown
8	“	Unknown (mainland Europe)	Unknown	“	“	“	“	“

Data from: \*Frei et al. (2009a): values from soil and snail shell; <sup>§</sup>Frei and Frei (2011): values from surface water; <sup>†</sup>Henderson et al. (1994); <sup>‡</sup>Voerkelius et al. (2010): values from mineral water. \*\*Longer-buried samples were too degraded to provide adequate mass for analysis.

### 2.5. Sample analysis

Sr isotope ratios were measured on a ThermoElectron Triton plus Thermal Ionization Mass Spectrometer (TIMS) at the Petrology department of the VUA. The Sr fractions were loaded onto Re filaments using a TaCl<sub>5</sub> activator to enhance ionization (Font et al., 2012).

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios were measured using a static multi-collection routine. An analysis consisted of 20 blocks of 10 cycles with an integration time of 8 s per cycle.  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios were corrected for mass fractionation using an exponential law and  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194 (Faure, 1986, 589).

The bulk of the analyses were carried out in 2011 when 58 analyses of the international Sr standard NBS987 were carried out on load sizes ranging from 10 ng to 100 ng to monitor and document the system's performance. The 10 ng average  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios for the NBS987 measurements were  $0.710242 \pm 0.000016$  (2SD) and  $0.056493 \pm 0.000008$  (2SD), respectively. The 100 ng average  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios for the NBS987 measurements were  $0.710242 \pm 0.000008$  (2SD) and  $0.056492 \pm 0.000004$  (2SD), respectively. The precision of concentration measurements was <0.09 ppm in experimental samples, and <0.35 ppm in archaeological samples. Final analyses in 2013 were combined with 4 standards, which were within error of the 2011 standards.

## 3. Results

Sample results are presented in Table 4, and blanks in Table 5. Total procedural blanks for Sr in the laboratory are generally below 100 pg. In this study they were variable, with one procedural blank yielding 400 pg. Maximum calculated contribution of blank Sr to sample total was 0.3%. Given the large range of Sr isotope variation in the samples, no blank correction was applied.

**Table 3**

Textile sample Sr cleaning methods employed.

Method	Reference	Samples treated	Fraction tested
No cleaning treatment	N/A	1–6	Residue
High pressure N <sub>2</sub> (g)	(Font et al., 2007)	1–8	Residue
HF(aq) 20%	(Frei et al., 2009a)	1–8	Residue
HF(aq) 20% + ammonium persulfate	(Frei et al., 2010)	2,4,6	Residue and leach
Organic solvents (MeOH/DCM) + H <sub>2</sub> O	(Hedges et al., 2005, cf von Carnap-Bornheim et al., 2007)	1–8	Residue

### 3.1. Control samples: effects of dyeing and cleaning

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios for dyed controls were less radiogenic (range 0.70847–0.70882) than those for undyed controls (range 0.71171–0.71177; Fig. 2a). Sr content was much higher and more variable in dyed samples (0.14–8.9 ppm) than in undyed samples (0.07–0.29 ppm, i.e. a difference of +1200 to +4200%, depending on cleaning method; Fig. 3b and c). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of dyed samples were within the range previously measured in soil leachates at the site where they were dyed (0.70761–0.70961; Frei et al., 2009a).

### 3.2. Experimental soil burials: effect of burial

On average, soil-buried samples had higher Sr content than the unburied controls described in Section 3.1 (range –75 to 3192%; Fig. 3b), but there was significant variation depending on location of burial and previous dyeing. Samples buried in a fenland bog (0.35–2.9 ppm) recorded a narrower range of Sr concentration than control samples (0.07–8.9 ppm) or samples buried in a marine environment (0.11–15.0 ppm; Fig. 3a). Buried dyed samples had higher Sr concentrations than buried undyed samples (0.34–15.0 ppm vs. 0.11–5.4 ppm). Because dyed samples had higher starting concentrations of Sr, buried dyed material showed smaller % changes in Sr content during burial (range –75 to +270% vs. –25 to +3192%).

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios in all buried samples were equal to or greater than their respective unburied controls (Fig. 2a), with the exception of uncleaned undyed samples that were less radiogenic than controls (Fig. 2b). The two uncleaned samples from the fenland bog closely resembled each other in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (undyed 0.71119 and dyed 0.71086) but the two uncleaned samples from marine sediment did not (undyed 0.71084 and dyed 0.71255). Buried samples showed more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than those expected for their local burial environments (Fig. 2a) based on either local environmental samples (fenland bog: 0.70761–0.70961; Frei et al., 2009a) or literature values (marine sediment/seawater:  $0.709158 \pm 0.000002$ ; Henderson et al., 1994).

### 3.3. Experimental soil burials: effects of cleaning methods

Sr concentration in uncleaned buried wool samples were typically less than 6 ppm (Fig. 3c). Samples cleaned with N<sub>2</sub> had Sr concentrations lower or comparable to those of their uncleaned moieties (% change –97 to –1%). Samples cleaned with HF(aq) all had lower Sr contents than uncleaned controls (<6 ppm; % change –64 to –49%), and those treated using HF(aq) plus a strong



**Table 4**

Sr isotope and elemental abundances in wool samples. – indicates not measured.

Sample no	Type	Burial site (years)	Dye/mordant	Cleaning method	Fraction analysed	Sample mass/g	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2 \text{ SE( abs)}$	Sr concentration (ppm)	Sr content ( $\mu\text{g}$ )
1	Control	N/A	None	Uncleaned	Residue	0.083	$0.71174 \pm 0.00001$	0.292	24.31
				N <sub>2</sub> (g)	Residue	0.192	$0.71171 \pm 0.00011$	0.207	39.64
				HF(aq)	Residue	0.201	$0.71176 \pm 0.00007$	0.082	16.37
				HF(aq)	Leach	0.201	$0.71188 \pm 0.00019$	0.114	22.80
				Organic solvents	Residue	0.071	$0.71177 \pm 0.00024$	0.067	4.77
				HF(aq) + oxid	Residue	–	–	–	–
2	Control	N/A	Madder/alum	HF(aq) + oxid	Leach	–	–	–	–
				Uncleaned	Residue	0.068	$0.70867 \pm 0.00001$	4.697	321.2
				N <sub>2</sub> (g)	Residue	0.134	$0.70878 \pm 0.00013$	8.919	1198
				HF(aq)	Residue	0.303	$0.70882 \pm 0.00015$	1.454	440.6
				HF(aq)	Leach	0.303	$0.70891 \pm 0.00015$	3.122	945.9
				Organic solvents	Residue	0.216	$0.70871 \pm 0.00009$	0.904	195.5
3	Experimental burial	Lejre, DK (1)	None	HF(aq) + oxid	Residue	0.059	$0.70847 \pm 0.00001$	0.143	8.46
				HF(aq) + oxid	Leach	0.059	$0.70868 \pm 0.00002$	0.307	18.21
				Uncleaned	Residue	0.041	$0.71119 \pm 0.00001$	1.120	45.36
				N <sub>2</sub> (g)	Residue	0.018	$0.71162 \pm 0.00017$	1.021	18.57
				HF(aq)	Residue	0.016	$0.71416 \pm 0.00011$	0.573	9.31
				HF(aq)	Leach	0.016	$0.72099 \pm 0.00011$	1.446	23.51
4	Experimental burial	Lejre, DK (1)	Madder/alum	Organic solvents	Residue	0.098	$0.71301 \pm 0.00013$	0.535	52.45
				HF(aq) + oxid	Residue	–	–	–	–
				HF(aq) + oxid	Leach	–	–	–	–
				Uncleaned	Residue	0.071	$0.71086 \pm 0.00001$	2.849	202.3
				N <sub>2</sub> (g)	Residue	0.022	$0.71121 \pm 0.00020$	2.186	48.54
				HF(aq)	Residue	0.016	$0.71341 \pm 0.00026$	1.288	20.74
5	Experimental burial	Marstrand, SE (3)	None	HF(aq)	Leach	0.016	$0.71910 \pm 0.00010$	1.778	28.65
				Organic solvents	Residue	0.031	$0.71061 \pm 0.00007$	0.834	25.52
				HF(aq) + oxid	Residue	0.066	$0.71774 \pm 0.00001$	0.353	23.36
				HF(aq) + oxid	Leach	0.066	$0.71862 \pm 0.00001$	1.170	77.41
				Uncleaned	Residue	0.013	$0.71084 \pm 0.00001$	5.386	71.15
				N <sub>2</sub> (g)	Residue	0.732	$0.71163 \pm 0.00014$	0.156	114.2
6	Experimental burial	Marstrand, SE (3)	Madder/alum	HF(aq)	Residue	0.032	$0.71637 \pm 0.00018$	2.686	86.54
				HF(aq)	Leach	0.032	$0.72132 \pm 0.00014$	2.739	88.25
				Organic solvents	Residue	0.021	$0.71790 \pm 0.00082$	0.111	2.30
				HF(aq) + oxid	Residue	–	–	–	–
				HF(aq) + oxid	Leach	–	–	–	–
				Uncleaned	Residue	0.028	$0.71255 \pm 0.00001$	15.013	415.0
7	Archaeological	Reykholt, IS (c. 500)	Unknown	N <sub>2</sub> (g)	Residue	0.013	$0.70998 \pm 0.00013$	14.852	196.0
				HF(aq)	Residue	0.012	$0.71104 \pm 0.00008$	5.374	65.84
				HF(aq)	Leach	0.012	$0.71173 \pm 0.00011$	16.817	206.0
				Organic solvents	Residue	0.006	$0.71010 \pm 0.00025$	1.880	10.34
				HF(aq) + oxid	Residue	0.041	$0.71093 \pm 0.00001$	0.338	14.01
				HF(aq) + oxid	Leach	0.041	$0.71178 \pm 0.00001$	10.323	427.5
8	Archaeological	Reykholt, IS (c. 500)	Unknown	Uncleaned	Residue	–	–	–	–
				N <sub>2</sub> (g)	Residue	0.029	$0.70428 \pm 0.00009$	36.411	1056
				HF(aq)	Residue	0.088	$0.70357 \pm 0.00001$	117.587	10,339
				HF(aq)	Leach	0.088	$0.70377 \pm 0.00019$	2.146	189
				Organic solvents	Residue	0.016	Failed	–	–
				HF(aq) + oxid	Residue	–	–	–	–
9	Archaeological	Reykholt, IS (c. 500)	Unknown	HF(aq) + oxid	Leach	–	–	–	–
				Uncleaned	Residue	–	–	–	–
				N <sub>2</sub> (g)	Residue	0.008	$0.70437 \pm 0.00014$	5.629	43.91
				HF(aq)	Residue	0.004	$0.70457 \pm 0.00016$	28.728	117.8
				HF(aq)	Leach	0.004	$0.70428 \pm 0.00013$	15.963	65.45
				Organic solvents	Residue	0.016	$0.70540 \pm 0.00016$	1.188	19.13
10	Archaeological	Reykholt, IS (c. 500)	Unknown	HF(aq) + oxid	Residue	–	–	–	–
				HF(aq) + oxid	Leach	–	–	–	–

oxidising agent showed even lower values (<1 ppm; % change –98 to –88%). The leaches from both HF cleaning methods contained more Sr per gram of original sample than the wool fibre residues (up to 18 ppm). Samples cleaned with organic solvents showed Sr concentrations below 2 ppm (% change –98 to –52%). Most cleaning series, including controls, showed an outlying sample with considerably more Sr content than the median: in all cases this was sample 6.

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios in buried samples were highly variable between cleaning series (difference between aliquots 0.00106–0.00713; Fig. 2c). This was 20–120 times greater variability than for unburied control samples (Fig. 2a). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the leaches from

HF(aq) washes were consistently more radiogenic than those of the residues (Fig. 2b and c, Table 4).

In dyed material, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of buried samples were all more radiogenic (0.70998–0.71774) than those of unburied controls (0.70847–0.70891), whether cleaned or uncleaned (Fig. 2b). There was no consistent relationship between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of cleaned and uncleaned samples for any cleaning method. No cleaning method retrieved control values (range of differences: 0.00121–0.00928). In contrast,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in undyed samples did show some consistency in the effects of cleaning. All cleaned material had equally or more radiogenic values (0.71162–0.71790) than the unburied controls (0.71171–0.71177), while uncleaned

**Table 5**  
Sr isotope and elemental abundances in blanks.

Name	Content	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2 \text{ SE(abs)}$	Sr total (pg)
Total procedural	7N HNO <sub>3</sub>	$0.7094 \pm 0.0022$	395.6
Total procedural	HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> 1:1	$0.7091 \pm 0.0011$	32.9
Reagent	2:1 MeOH/DCM	$0.7092 \pm 0.0005$	413.2
Reagent	2:1 MeOH/DCM	$0.7091 \pm 0.0017$	203.6
Reagent	2:1 DCM/MeOH	$0.7084 \pm 0.0003$	195.3
Reagent	20% ammonium persulfate (aq)	$0.7102 \pm 0.0012$	197.5
Reagent	1 drop H <sub>3</sub> PO <sub>4</sub> + 4 drops HF + 1 mL HNO <sub>3</sub> + 1 mL H <sub>2</sub> O <sub>2</sub> + 5 mL H <sub>2</sub> O	$0.7113 \pm 0.0015$	23.2
Loading	Clean, degassed filament only	$0.7080 \pm 0.0025$	11.0

samples showed less radiogenic values (0.71119, 0.71084). Aliquots cleaned with compressed N<sub>2</sub> showed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that closely resembled control values (difference from control values: 0.00009–0.00015; Fig. 2b). Samples cleaned with organic solvents and HF(aq) showed greater differences (range: 0.00124–0.00619).

### 3.4. Archaeological textiles

Compared to the experimentally buried textiles, the archaeological samples had a wider range and generally higher values of Sr content (1.2–118 ppm; Fig. 3a). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of both samples 7 (typical of Icelandic manufacture) and 8 (atypical of Icelandic manufacture but typical of some contemporary mainland European industries) did not differ greatly between cleaning methods (range

0.00071–0.00103; Fig. 2a). Both samples showed un-radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, all within the range observed in Icelandic groundwaters, and most below the range observed in animal and plant tissues from Iceland.

## 4. Discussion

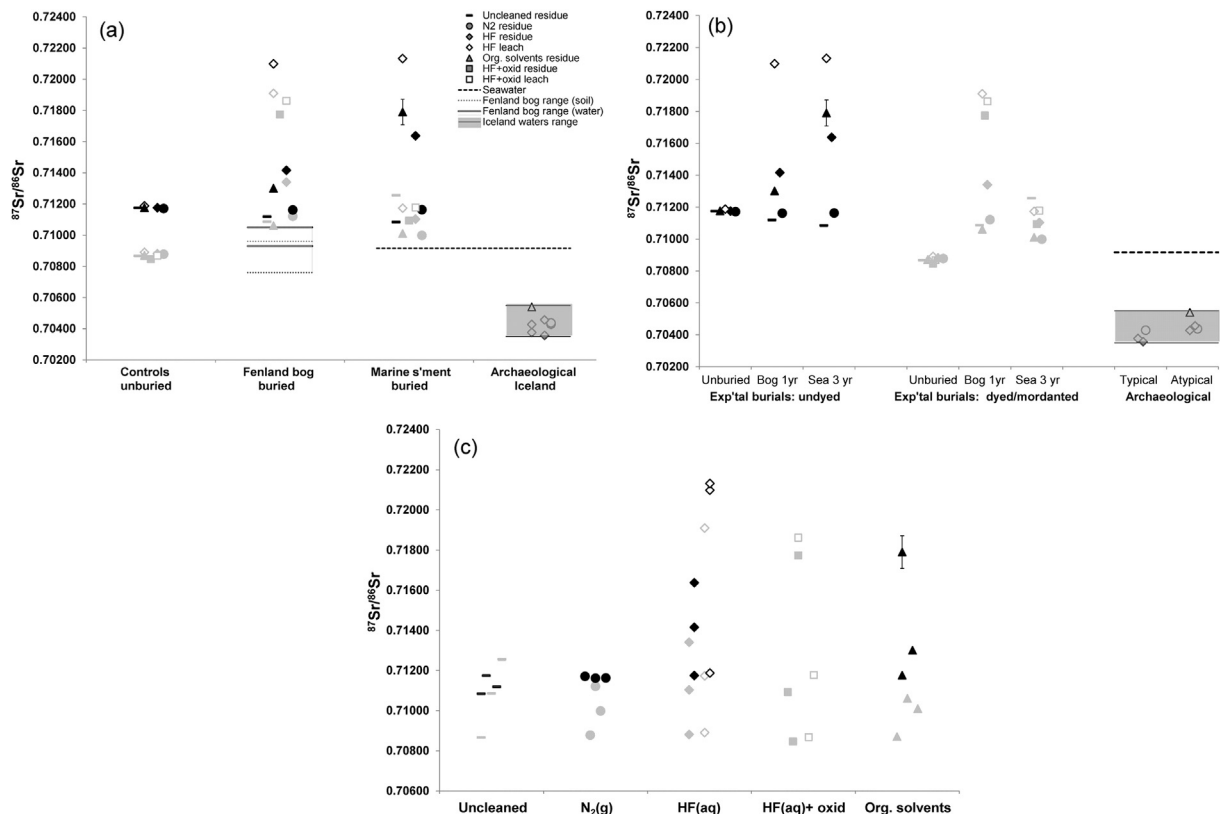
### 4.1. Blanks

Sr content of blanks for the tested procedures ranged by an order of magnitude. Nevertheless, the maximum calculated contribution of solvent or procedure-derived Sr was insufficient to lead to significant changes in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the wool and leachate samples. Results from textile samples were therefore not significantly affected by blank contributions.

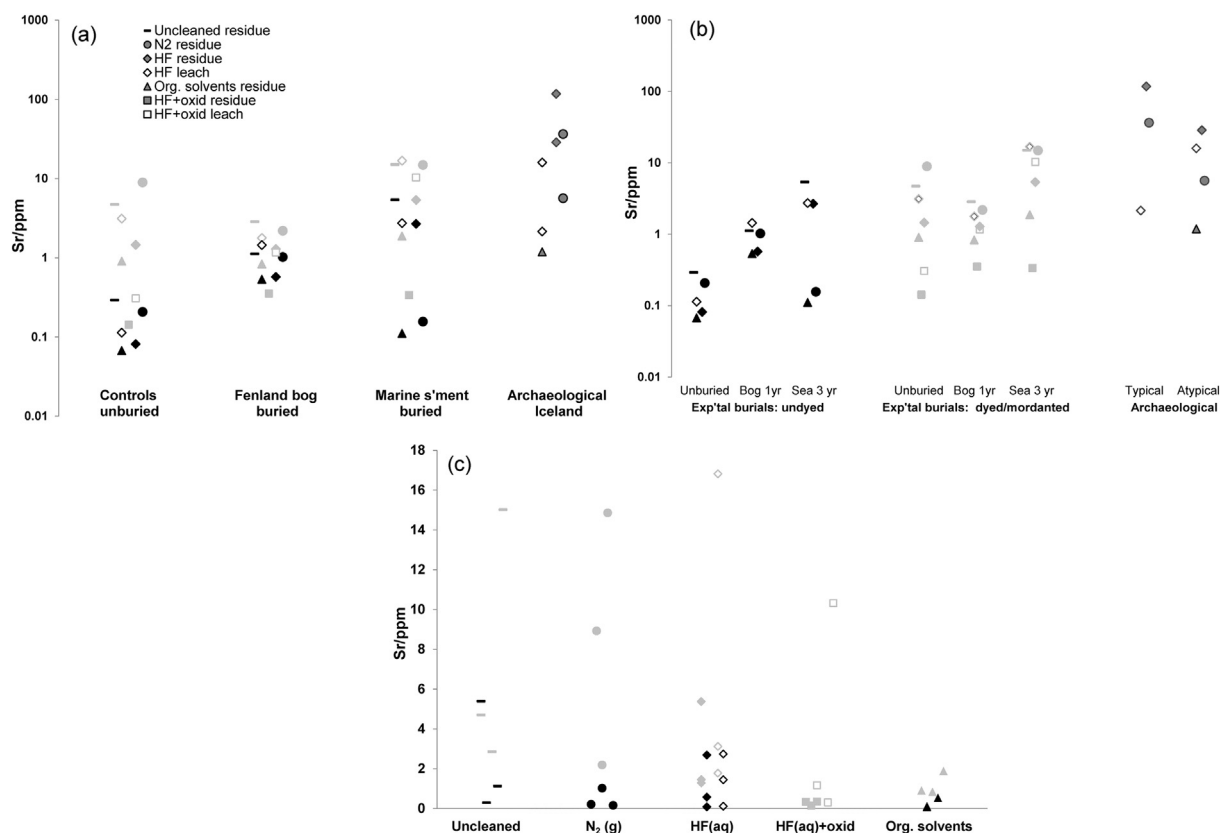
### 4.2. Unburied samples: effect of dyeing

Dyeing/mordanting made a significant contribution to both the Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of unburied wool textile samples (Figs. 2 and 3). The concentration of Sr in dyed/mordanted control samples was 1200–1700% higher than that recorded in undyed samples (Table 4), and was also more variable (range 8.7 ppm vs. 0.2 ppm). Variability in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios was however small (maximum in dyed samples 0.00035,  $n = 4$ ; in undyed samples 0.00006,  $n = 5$ ), despite the differing cleaning methods used. This indicated that the original undyed and dyed samples each had homogenous but distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios.

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios in wool sample residues were consistently lower in dyed/mordanted samples than in undyed samples (difference



**Fig. 2.**  $^{87}\text{Sr}/^{86}\text{Sr}$  values for all samples by (a) burial site; (b) pre-burial treatment; and (c) cleaning method. Legends indicate marker shape: undyed samples black; dyed samples grey; archaeological samples bounded. Archaeological samples are not shown in (c). Environmental values for seawater are predicted (Table 2) rather than measured directly. Analytical errors are smaller than the size of the symbols except for sample 6, organic solvent residue ( $\pm 2 \text{ SE (abs)}$ ).



**Fig. 3.** Sr concentration (ppm) for samples by (a) burial site; (b) pre-burial treatment; and (c) cleaning method. Values in (a) and (b) plotted on logarithmic scale. Legend indicates marker shape: undyed samples in black; dyed samples in grey; archaeological samples are bounded. Archaeological samples are not shown in (c).

0.00289–0.00330). This uniformity suggested that material from the dyeing/mordanting process was the dominant source of Sr in the dyed samples. This could derive from dye, mordant or dye-bath water. Madder is of vegetable origin, as are many historically-used dyestuffs (Ferreira et al., 2004). The Sr content of plants varies by species and lies between 0 and 1500 ppm (Kabata-Pendias and Pendias, 2001, 128). Historically-used mordants were one of a small number of mineral ores, which can have highly variable trace element contents depending on their specific genesis (Sr 6–1900 ppm: Turekian and Kulp, 1956). Both dyes and mordants were traded extensively in the past (e.g. Jecock, 2009; Spufford, 2006, 334) and thus neither may be local to the site of production of a wool fibre. The water in the dye-bath will itself contain a contribution of Sr from local sources. Unfortunately, neither the origin nor the Sr content of the original dye and mordant used in this study were recorded (Peacock, 2004). However the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of sheep wool, soil leachates (Frei et al., 2009a) and surface water (Frei and Frei, 2011) at the dyeing/mordanting site have been well characterised.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of unburi ed dyed samples in this study were consistent with values from soil leachates (range 0.70761–0.70961), which are systematically lower than values from surface water (range 0.70927–0.71053) or wool from locally-raised sheep (range 0.70931–0.71021; no cleaning treatment) for the same location (Frei and Frei, 2011; Frei et al., 2009a).

#### 4.3. Unburied samples: effect of cleaning

All cleaning methods removed Sr from wool samples. Only the  $\text{N}_2$ -cleaned sample of dyed wool contained a greater concentration of Sr than its uncleaned moiety. This result is most likely to indicate inherent variability in Sr content (but not  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, see Section

4.2) in unburi ed dyed samples. Given that the different cleaning techniques used here are likely to remove Sr from different parts of the wool (particulate, lipid-, or protein-bound), these data indicate that: (1) all binding sites in both dyed and unburi ed fibres were occupied by Sr of approximately the same  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio; and (2) no cleaning method introduced enough exogenous Sr to alter wool sample  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. In dyed samples, none of the cleaning methods retrieved pre-dyeing  $^{87}\text{Sr}/^{86}\text{Sr}$  composition (Fig. 2b). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the unburi ed dyed samples therefore provided no information about their provenance.

#### 4.4. Experimental soil burials: effect of burial

Burial in a marine environment significantly increased Sr content over unburi ed controls (–25 to +3192%) whilst fenland bog burial had a smaller effect (–75 to +695%; Fig. 3a). The burial-degraded textiles used in this study have been shown to have undergone some peptide change (Solazzo et al., 2013) though this was not enough to significantly change the overall amino acid content of the fibre (von Holstein et al., 2014). Therefore, the number and nature of Sr binding sites in the protein fraction of the fibre is likely to differ little between controls and seawater- or bog-buried samples. We hypothesise therefore that the difference in Sr uptake between sites was instead related to the higher Sr content of seawater (c. 8 ppm: Veizer, 1989) compared to fenland groundwater (c. 0.3 ppm: Frei and Frei, 2011) and/or the more neutral pH in the marine burial (7.2–7.5 vs. 5.6; Solazzo et al., 2013), leading to precipitation of Sr-containing mineral phases.

Buried samples showed a wider range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than unburi ed samples, despite having been cleaned by the same range of methods. Buried samples were much smaller than controls, so

this effect may be due to highly local  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio variation in the burial environment and hence retrieved samples. It is also possible, however, that this variation relates to highly variable responses of the Sr derived from burial to cleaning methods.

The contribution from the dyeing/mordanting process to the Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of wool samples remained dominant after burial and washing. Each dyed/mordanted sample was less radiogenic and contained more Sr than its undyed moiety (true for all but one cleaning method pair: Figs. 2b and 3b). The exception was the uncleaned aliquots from marine sediment (5 and 6), where the undyed sample had higher  $^{87}\text{Sr}/^{86}\text{Sr}$  than the dyed sample (difference 0.00171), possibly due to inhomogeneity in sediment  $^{87}\text{Sr}/^{86}\text{Sr}$  values at the site.

All  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in buried samples were more radiogenic than expected from their environments: those from a marine environment were more radiogenic than the literature average for seawater, and those from the fenland bog higher than directly measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from surface waters, soil leachates, snail shell and (non-HF treated) sheep wool (Frei and Frei, 2011; Frei et al., 2009a). The result from the marine environment is not necessarily significant as marine sediment  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were not measured and Sr introduced during burial will be derived from both seawater and the enclosing sediments (Table 1). At both sites, Sr absorbed by wool samples may have been affected by the well-documented differential weathering processes affecting environmental Sr ratios (Blum et al., 1993; Blum et al., 2000). Alternatively, it is possible that only part of the Sr present in the samples was accessible to the dissolution procedure. This phenomenon was, however, not observed in the unburied controls, which were significantly larger than buried samples. This effect cannot therefore have been due to sample size, but instead to the binding of the dominant contribution of Sr from the burial environment, possibly interacting with the effects of cleaning.

#### 4.5. Experimental soil burials: effect of cleaning procedures

All cleaning methods decreased Sr content of the residue (Fig. 3c). This effect was also noted in a comparison of washing procedures for human hair (Tippie et al., 2013).

##### 4.5.1. Cleaning with $\text{N}_2$

Samples that were cleaned with compressed  $\text{N}_2$  contained similar concentrations of Sr to uncleaned samples. For undyed samples,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios closely resembled values from unburied controls (differences from control values: 0.00009–0.00015). This was not the case for dyed samples (differences from control values: 0.00117–0.00274). These data suggest that most of the diagenetic Sr deposited during burial is present as particulates, which are removed by high-pressure gas treatment. However, contributions from the dyeing/mordanting process were not effectively removed by this cleaning treatment. We conclude that Sr from dye/mordant is therefore likely to be additionally bound to other fractions of the wool fibre.

##### 4.5.2. Cleaning with HF(aq)

Cleaning with HF(aq) removed Sr from the wool fibre in both dyed and undyed samples, and the addition of a strong oxidising agent increased the efficacy of this process (Fig. 3c). We hypothesise that HF(aq) removed exogenous particulates by dissolution, and also lipid-bound Sr (Frei et al., 2009a) but possibly also that bound exchangeably to the protein. The strong acid and/or oxidising agent may have additionally destroyed a number of the binding sites for Sr in the fibre, or oxidised bound Sr sulfides to soluble Sr sulfates. We consider this interpretation more likely than an interior/exterior differentiation (cf. Tippie et al., 2013).  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios

of both dyed and undyed samples treated with HF(aq) (with or without the addition of a strong oxidising agent) did not resemble those of unburied controls (difference range: 0.0022–0.0093).

It is clear that an isotopic imbalance occurred in this procedure. For undyed buried samples, and for the dyed sample buried in fenland bog, the total  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for this procedure (the weighted average of residue and leach fractions) was more radiogenic than in both unburied and uncleaned controls. This effect may have been a mass balance issue, present to a degree in all cleaning procedures, but only evident in HF treatment because both residue and leach were analysed. Sr concentration was, however, so variable between textile samples that the loss of Sr during the dissolution process cannot be shown.

It has previously been suggested that the  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of the leachate from the cleaning procedure with HF(aq) with a strong oxidising agent represents the contribution from the dyestuff and therefore, the origin of this material (Frei et al., 2010). Results from this study do not support this conclusion, at least for madder-dyeing/alum-mordanting. In unburied samples,  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of leachates did not differ significantly from residue (Fig. 2b, Table 4). In buried samples, these values were consistently much higher than unburied control values. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the leachates therefore told us nothing about the provenance of dye or mordant, or the location of dyeing.

##### 4.5.3. Cleaning with organic solvents

Samples cleaned with organic solvents (DCM/MeOH/ $\text{H}_2\text{O}$ ) contained less Sr than all other methods except HF(aq) + oxidising agent. The efficacy of this procedure was greater than expected, given that only c. 20% endogenous Sr is present in the lipid fraction of hair (Attar et al., 1990). In addition to removing the lipid-bound Sr, we suggest that this procedure, which included six sonications with solvent, removed Sr in contaminant particulates by agitation or dissolution. In all buried samples treated with this method, as for samples cleaned with HF(aq),  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were higher than in controls, but did not show any consistent relationship to samples in other cleaning series. These differences could not be explained by contamination during cleaning (Table 5).

#### 4.6. Archaeological textiles

Both archaeological samples contained higher concentrations of Sr than experimentally buried textiles (Fig. 3a). This is consistent with previous data for  $\text{Ca}^{2+}$  concentrations in buried mammalian hair fibres (Kempson et al., 2003; Peacock, 1996) and is most likely due to greater exposure time to groundwater. It was not possible, however, to exclude the possibility that part of this Sr may be derived from (1) pre-burial dyeing/mordanting, as the presence of dyes/mordants was not directly tested in these samples, or (2) post-excavation washing with tap water, though this was unlikely to have contained greater quantities of Sr than groundwater.

After cleaning, both archaeological samples showed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios within a narrower range (0.00071–0.00103) than experimentally-buried samples (Fig. 2b). All  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were consistent with Icelandic groundwater values.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were lower than expected for sample 7 (typical of Icelandic manufacture), showing no contribution from marine Sr sources, as do other animal and vegetable tissues from Iceland. It was also inconsistent with expectations for sample 8 (atypical of Icelandic origin), as these isotopic ratios are very rare in groundwater from mainland Europe, and are unknown in animal and vegetable tissues from this region (Voerkelius et al., 2010). These values are most likely to reflect the contribution from local groundwater during burial, though a contribution from post-excavation washing cannot be



excluded. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of archaeological wool samples cleaned in the methods tested in this study were therefore inconsistent with expected wool provenance, and strongly suggested that the additional Sr in these samples was derived from the burial environment.

## 5. Conclusion

This study directly tested the effect of wet soil burial on the Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of wool fibres. The results show that both dyeing/mordanting and wet soil burial can change these analytical parameters. In unburied samples (dyed and undyed), all binding sites of the fibre (protein, lipids, particulates, and possibly melanin or other sites) were occupied with Sr of the same isotopic composition, which was removed to differing extents by cleaning methods. Sr content in buried samples was highly variable, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were generally higher than in unburied controls, and also more radiogenic than expected from their burial environments. It is possible that part of the Sr present in the buried samples remained inaccessible to the dissolution procedures employed. Nevertheless, high pressure  $\text{N}_2$  cleaning (Font et al., 2007) accurately retrieved original  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in buried undyed samples, suggesting that most exogenous Sr present in these samples was in particulate form. In dyed/mordanted samples, no cleaning method tested consistently retrieved original  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Results from archaeological samples suggested the presence of exogenous Sr derived from water in the burial environment in all Sr pools in the fibre. The sensitivity of wool Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio to dyeing, burial and cleaning procedures was consistent with the previously established affinity of wool for heavy metal cations and the variable response of wool-bound metal cations to solvents.

The application of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio provenancing to archaeological samples of wool textile is therefore problematic because:

1. The contribution of Sr from the burial environment and dyeing/mordanting appears to be not consistently removable, at least with the methods tested here.
2. It is not possible to confidently identify samples that have never been subjected to dyeing/mordanting. A negative dye test indicates only that a sample at present contains no detectable level of organic dyestuff (e.g. Vanden Berghe et al., 2009), not that it has never been dyed.

Post-excavation conservation may additionally change Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios unless ultra-low blank reagents are used. However, provenancing undyed, unconserved and unburied wool, or wool which has been buried in dry soil environments, may still be robust. The same is true for provenancing other types of animal hair which have not been subject to extensive mechanical and/or chemical pre-treatment (Benson et al., 2006; Coutu, 2011; Font et al., 2012).

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